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Temperature Dependence of Vibrational Relaxation from the Upper Vibrational Levels of HF and DF

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A kinetic model of infrared laser-induced fluorescence experiments has been used to simulate quenching coefficients between 300 and 2400 K for the vibrational relaxation of $HF(v_1)$ and $DF(v_1)$ by $HF(v_2 = 0)$ and $DF(v_2 = 0)$. This rotational nonequilibrium model is based on the predicted energy-transfer mechanisms in hydrogen fluoride and deuterium fluoride systems reported earlier by Wilkins. The deactivation rates for the V→R processes for $HF(v_1) + HF(v_2 = 0)$ and their isotopic analogs are predicted to scale as v^n with n varying from 2.3 to 1.6 as v_1 varies from 2 to 6. These quenching coefficients for V→R processes from the

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20. ABSTRACT (Continued)

upper vibrational levels are predicted to have a temperature dependence very similar to that for $V \to R$ relaxation from the $v_1 = 1$ level. The results are discussed in relation to $V \to V$ energy transfer and $V \to R$ intramolecular energy conversion.

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I. INTRODUCTION

Measured temperature-dependent quenching coefficients for collisional deactivation of HF($v_1 = 1$) and DF($v_1 = 1$) molecules by HF($v_2 = 0$) or DF($v_2 = 0$) molecules are available because these systems have been studied extensively.[1] There is, however, a scarcity of temperature-dependent quenching coefficients for collisional deactivation of HF species and HF isotopic species from vibrational states above the first vibrational level. The deactivation from the upper vibrational levels of HF and DF by HF($v = 0$) or DF($v = 0$) at room temperature has been studied experimentally by direct laser pumping of the $v = 2$ or $v = 4$ vibrational levels of HF,[2,3] low-pressure combustion in a flow cell,[4,5] reactive flows in medium-pressure flow tubes,[6-8] high-temperature combustion in shock tubes,[9] and laser-induced fluorescence by sequential photon absorption.[10-13]

In a recent paper, Wilkins and Kwok[14] presented a kinetic model of infrared laser-induced fluorescence experiments, which simulated available experimental data for vibrational relaxations of HF($v_1 = 1$) + HF($v_2 = 0$) and its isotopic analogs.[15,16] That rotational nonequilibrium model was based on the predicted energy-transfer mechanism in HF systems reported in a trajectory study by Wilkins.[17] The model explained the temperature dependence observed for HF($v_1 = 1$) vibrational relaxation by HF($v_2 = 0$). In fact, the entire temperature dependence of the reported quenching rate coefficients was explained without use of any mechanisms that involve dimerization.

In the previous trajectory study[17] on HF(v_1) + HF($v_2 = 0$) collisions, the following conclusions were drawn:

1. For HF(v) + HF collisions, the most probable paths for V → V exchange involve single vibrational quantum transitions.

2. The V → R processes occur by means of an intramolecular energy-transfer mechanism. The vibrationally excited HF molecule converts one or more quanta of its vibrational energy into rotational energy, thus populating its high rotational states.

3. One quenching process of the high rotational quantum states is the slow relaxation by R → (R',T') processes. The probability of rotational de-excitation decreases as rotational quantum J increases. At high values of J, J = ± 1 rotational transitions are much more probable than multiple quantum rotational transitions.

4. HF quasidimers formed at room temperature or above are not necessary to account for the fast V → R self-relaxation rates with inverse temperature dependences measured by various experimental techniques.

Additional trajectory studies[15,16] verified that the conclusions reached for the mechanisms in $HF(v_1)$ + $HF(v_2)$ collisions are equally applicable to $DF(v_1)$ + $DF(v_2)$ and $HF(v_1)$ + $DF(v_2)$ systems. The exception to these mechanisms involves the lack of V → V energy transfer in $DF(v_1)$ + $HF(v_2 = 0)$ systems. However, this result has been confirmed in laser-excited induced fluorescence experiments. The large endothermicities involved in $DF(v_1)$ + $HF(v_2 = 0)$ collisions probably prevent the occurrence of the V → V process. The collision dynamics indicate that in V → V transfer of $DF(v_1)$ + $HF(v_2)$ and $HF(v_1)$ + $DF(v_2)$ collisions, vibrationally excited $HF(v_1)$ molecules transfer vibrational energy to the DF molecules.

The previous three trajectory studies reached the following conclusions concerning V $\rightarrow$ V transfer:

1. In both $HF(v_1)$ + $HF(v_2 = 0)$ and $DF(v_1)$ + $DF(v_2 = 0)$ systems, the rate coefficients for the V $\rightarrow$ V processes decreased as v increased because of the increased endothermicities with increasing v.

2. In $HF(v_1)$ + $DF(v_2 = 0)$ collisions, the rate coefficients for V $\rightarrow$ V processes increased slightly as v increased because of the decrease in exothermicities with increasing v.

3. In $DF(v_1)$ + $HF(v_2 = 0)$ collisions, rate coefficients for V $\rightarrow$ V processes can be neglected, since they are calculated from small cross sections that result from their large endothermicities.

4. The rate coefficients for the V $\rightarrow$ V processes had a T^{-1} temperature dependence.

It is difficult to assess separate actual values for V $\rightarrow$ V or V $\rightarrow$ R processes from the experimental measurements, because measured coefficients usually represent the sum of the contributions from the V $\rightarrow$ V and the V $\rightarrow$ R energy-transfer processes for many transfer channels.

In addition, the calculated[15-17] temperature-dependent rate coefficients cannot be compared directly with the experimental temperature-dependent rate coefficients for the vibrational deactivation of $HF(v_1)$ or $DF(v_1)$ by either $HF(v_2 = 0)$ or $DF(v_2 = 0)$. The latter should be called "empirical quenching coefficients," since they represent net removal rates of $HF(v_1)$ or $DF(v_1)$ through a number of energy-transfer channels. Previous experimental analyses of deactivation of these species from upper vibrational states did not properly consider the role of V $\rightarrow$ R and R $\rightarrow$ V energy-transfer processes.

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The latter mechanisms are believed to be important in the vibrational deactivation of hydrogen halides, particularly HF and its isotopic species, from upper vibrational levels. Most current experimental methods are not capable of directly measuring the fine structure rate coefficients for the energy-transfer processes as predicted by the trajectory studies.

The rate coefficients for $V \rightarrow R$, $R \rightarrow V$, $R \rightarrow (T',R')$ and $(R',T'') \rightarrow R$ and $V \rightarrow V'$ energy-transfer processes obtained from the trajectory studies were incorporated into a nonequilibrium kinetic computer program that models the laser-induced fluorescence technique. The purpose of this study is to determine if this rotational nonequilibrium model can reproduce the experimental temperature-dependent quenching rate coefficients for vibrational deactivation of $HF(v_1 = 2 \text{ to } 6)$ by $HF(v_2 = 0)$, $HF(v_1 = 2 \text{ to } 6)$ by $DF(v_2 = 0)$, $DF(v_1 = 2 \text{ to } 6)$ by $DF(v_2 = 0)$, and $DF(v_1 = 2 \text{ to } 6)$ by $HF(v_2 = 0)$. The quenching rate coefficients for the $V \rightarrow R$ processes are obtained by subtracting the rate coefficients for the approximate $V \rightarrow V$ processes from the total decay rate (i.e., $k_T = k_{VV} + k_{VR}$). The deactivation rates for the $V \rightarrow R$ processes are then used to determine how $V \rightarrow R$ rates scale with vibrational level v.

II. MODEL

In a previous paper, Wilkins and Kwok[14] described the computer code developed to calculate time-dependent $HF(v_1, J_1)$ concentrations in defined vibrational (v_1) and rotational (J_1) states for specific kinetic experiments relevant to energy transfer in HF. The description of the model presented in that paper will not be repeated here. The model is extended to higher v_1 levels by incorporation of the additional fine structure rate coefficients for $V \to R$, $R \to V$, $R \to (R',T')$ and $(R',T') \to R$ and $V \to V'$ obtained from the trajectory studies.[15-17] In the appendices are tabulated rate coefficients employed in the model calculations. The rate coefficients for rotational relaxation are assumed identical in each of the v_1' manifolds. The NEST code[18] is used to calculate the rotational nonequilibrium effects. Time-dependent $HF(v_1, J_1)$ densities must be generated by this model for comparison with actual experiments. The computer number densities are summed over J, and the sum is analyzed in the same manner as in actual experiments to deduce the empirical quenching coefficients reported by experimenters (generally for room temperature).

The computer model employed to obtain total decay rates for relaxation from the upper vibrational levels of $HF(v_1)$ simulates a novel variation of the method of laser-induced fluorescence.[10] The experimental technique involves exciting the first, the first and second, the first, second, and third, etc. vibrational levels of HF with the use of multiband laser optical pumping. The vibrational level of interest is then populated by collisions of the photolytically excited HF species. The mathematical model presented by Osgood,

Sackett, and Javan[10] is used here. They demonstrated that the temporal
evolution of $n_v(t)$ can be written as

$$n_v(t) = A(1 - e^{-t/\tau_R}) e^{-v\gamma_1 t} \qquad (1)$$

where A is a constant, τ_R is the risetime, and γ_1 is the decay rate from the
$v_1 = 1$ level. The temporal behavior of n_v is described by a factor with a
rising exponential whose time constant is essentially the total decay rate for
de-excitation from level v times a factor with an exponential decay rate v
times the V → R decay rate from the v = 1 level. τ_R is defined by

$$\frac{1}{\tau_R} = k_{vv} + k_{vR} - v\gamma_1 = k_T - v\gamma_1 \qquad (2)$$

where

$$k_T = k_{vv} + k_{vR} = \frac{1}{\tau_R} + v\gamma_1 \qquad (3)$$

and k_T is the total decay rate from level v, k_{vv} is the contribution to k_T
from V → V energy-transfer processes, and k_{vR} is the contribution to k_T from V →
R processes. To obtain τ_R, the time at which the maximum fluorescence
intensity occurs is measured. The equivalent is obtained theoretically by
solving for the point in time at which $n_v(t)$ is a maximum. Setting $dn_v(t)/dt$
equal to zero, and solving for t_{max} we obtain

$$t_{max} = \tau_R \ln \left(1 + \frac{\tau_d(v)}{\tau_R} \right) \qquad (4)$$

where the decay time $\tau_d(v) = 1/v\gamma_1$. The risetime τ_R is obtained by solving the transcendental equations numerically. This technique is applicable as long as $\tau_R \ll \tau_d$.

The initial conditions for each computation depend on proper adjustment of the laser-excited population of the levels n_v^o. Osgood, Sackett, and Javan[10] demonstrated that the time-dependent amplitudes of n_v at vibrational equilibrium are defined by

$$n_v^o = \left(\frac{n_1^o}{n_o}\right)^{v-1} \cdot n_1^o \exp\left[\frac{2\omega_e X_e}{kT} \sum_{j=1}^{v} (j - 1)\right] \qquad (5)$$

where $\omega_e x_e$ is the anharmonicity constant for the diatomic molecule. This choice of n_v^o removes all dependence on the previously measured $k_{VV} + k_{VR}$ and decouples the behavior of the vth level from that of all higher vibrational levels. At a given temperature, pressures of $HF(v_2 = 0) = \sum_{J_2} [HF(v_2 = 0, J_2)]$ up to 0.5 Torr are used. In the nomenclature of Osgood, Sackett, and Javan, n_1^o/n_o was taken to be 0.01 at temperatures from 300 to 700 K, 0.1 from 700 to 1400 K, and 0.2 from 1600 to 2400 K.

As in our previous simulation,[14] extreme care has been taken to duplicate the reported initial conditions of the experiments [Eq. (5)] as well as the interpretive approaches of the experimenters [Eqs. (1)-(4)] as we relate model number density results to their works. Then we extend the temperature range beyond that of their experiments.

III. RESULTS AND DISCUSSION

As with the actual experiments, the rise rate τ_R is obtained from Eq. (4). The calculation is performed at several HF densities to verify that the total decay rate $(k_{vv} + k_{vR})$ is the result of HF quenching. The slope of the inverse characteristic decay times versus HF(v = 0) densities yields the same computed value of $k_{vv} + k_{vR}$. This process has been used by experimenters to ensure that the deduced observed quenching coefficient $k_{vv} + k_{vR}$ is not affected by competing secondary processes.

Table I presents a summary of the number of species HF(v_1, J_1) and rate coefficients for the different energy-transfer processes involved in the use of this method to compute the total decay rate from the v = 3 level of HF. A plot of a typical output from the computer for $n_v(t)$ with v = 1, 2, and 3 as a function of time is given in Fig. 1. From Fig. 1, $t_{max} = 5.0 \times 10^{-6}$ sec, $\tau_d(v = 1) = \gamma_1 = 2.5 \times 10^4 sec^{-1}$, $\tau_d(v = 2) = 5.0 \times 10^{-4} sec^{-1}$, and $\tau_d(v = 3) = 7.5 \times 10^4$ sec^{-1}. It was found that $\tau_d(v = 2)$ and $\tau_d(v = 3)$ were approximately $2\tau_d(v = 1)$ and $3\tau_d(v = 1)$, respectively. Application of Eq. (4) yields $\tau_R = 2.75 \times 10^{-6}$ sec and $k_{vv} + k_{vR} = 17.5 \times 10^{12}$ cm^3/mole sec. From the trajectory study,[17] k_{vv} for v = 3 at 300 K has a value of 5.2×10^{12} cm^3/mole sec. If we subtract k_{vv} from k_T, we obtain $k_{vR} = 12.3 \times 10^{12}$ cm^3/mole sec at room temperature. The inverse of the quenching coefficients for V → R processes for HF(v) + HF and its isotopic analogs is illustrated on traditional Landau-Teller plots in Figs. 2 through 5, where Pτ(v) is plotted as a function of $T^{-1/3}$. The model described by Wilkins and Kwok[14] replicated the empirical quenching coefficients for HF(v = 1) + HF relaxation. The model

TABLE I. Full kinetic model for HF(v) self-relaxation

Species Type	Species	V → R rate Coefficients	R → R rate Coefficients	V → V rate Coefficients	Rate Equations
HF(v = 1) + HF					
HF(v = 0, 0 < J < 16)	17	0	16	0	
HF(v = 1, 0 < J < 5)	6	42	5	0	
Total	23	42	21	0	63
HF(v = 2) + HF					
HF(v = 0, 0 < J < 21)	22	0	21	0	
HF(v = 1, 0 < J < 16)	17	42	16	0	
HF(v = 2, 0 < J < 16)	5	78	5	6	
Total	44	120	42	6	168
HF(v = 3) + HF					
HF(v = 0, 0 < J < 25)	26	0	25	0	
HF(v = 1, 0 < J < 20)	21	42	20	6	
HF(v = 2, 0 < J < 15)	16	78	15	6	
HF(v = 3, 0 < J < 5)	6	96	5	0	
Total	69	216	65	12	293

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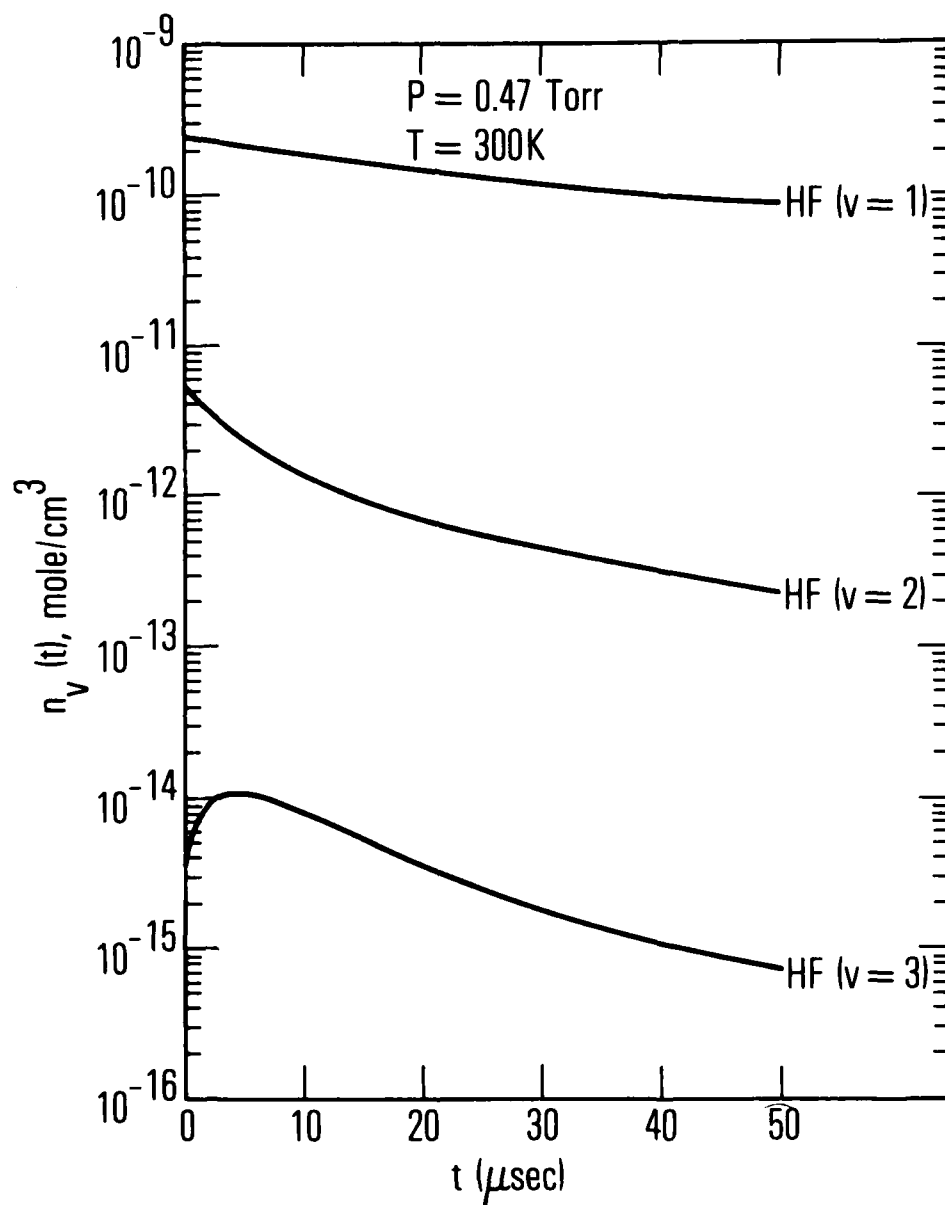
Fig. 1. Total decay rate from the v = 3 level of HF. Number density $n_v(t)$ versus t(µsec). The first and second vibrational levels of HF are excited by multiband laser optical pumping. The v = 3 level is populated by collisions of the photolytically excited HF species.

T (K)

3000 2400 1800 1400 1200 1000   700   500   300

$HF(v_1) + HF(v_2 = 0)$

$P\tau$ (μsec-atm)

10^{-1}

10^{-2}

10^{-3}

v = 1

v = 2

v = 3
v = 4
v = 5
v = 6

1

0.07   0.08   0.09   0.10   0.11   0.12   0.13   0.14   0.15

$T^{-0.33}$ (K)

Fig. 2.   Rate coefficients for vibrational relaxation of $HF(v_1 = 1$ through 6) by $HF(v_2 = 0)$. $P\tau$(μsec-atm) versus T and $T^{-1/3}$ with T in K.

Fig. 3. Rate coefficients for vibrational relaxation of DF(v_1 = 1 through 6) by DF(v_2 = 0). $P\tau(\mu sec-atm)$ versus T and $T^{-1/3}$ with T in K.

Fig. 4. Rate coefficients for vibrational relaxation of HF($v_1 =$ 1 through 6) by DF($v_2 = 0$). Pτ(μsec-atm) versus T and T$^{-1/3}$ with T in K.

Fig. 5. Rate coefficients for vibrational relaxation of $DF(v_1 = 1$ through 6) by $HF(v_2 = 0)$. $P\tau$(μsec-atm) versus T and $T^{-1/3}$ with T in $^{\circ}K$.

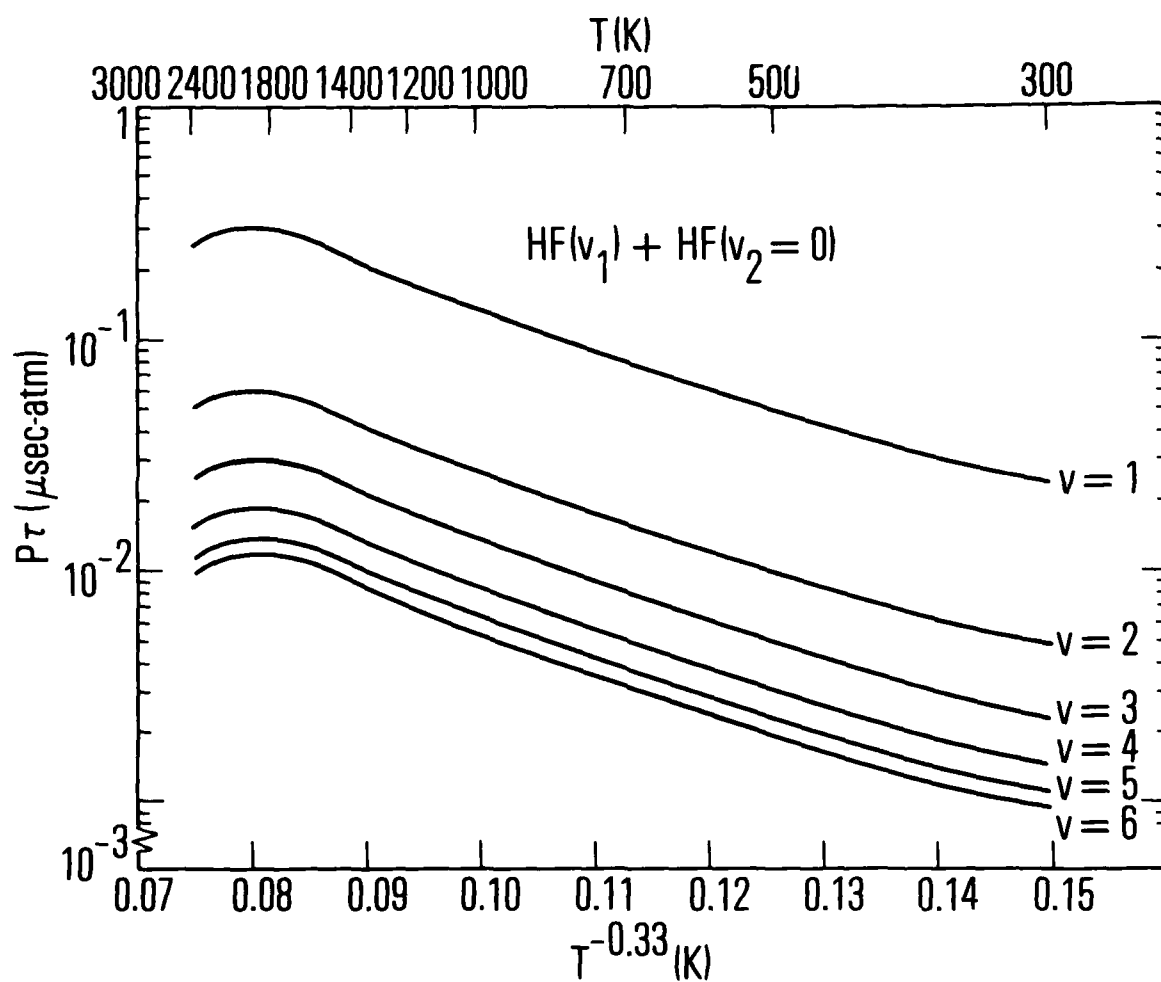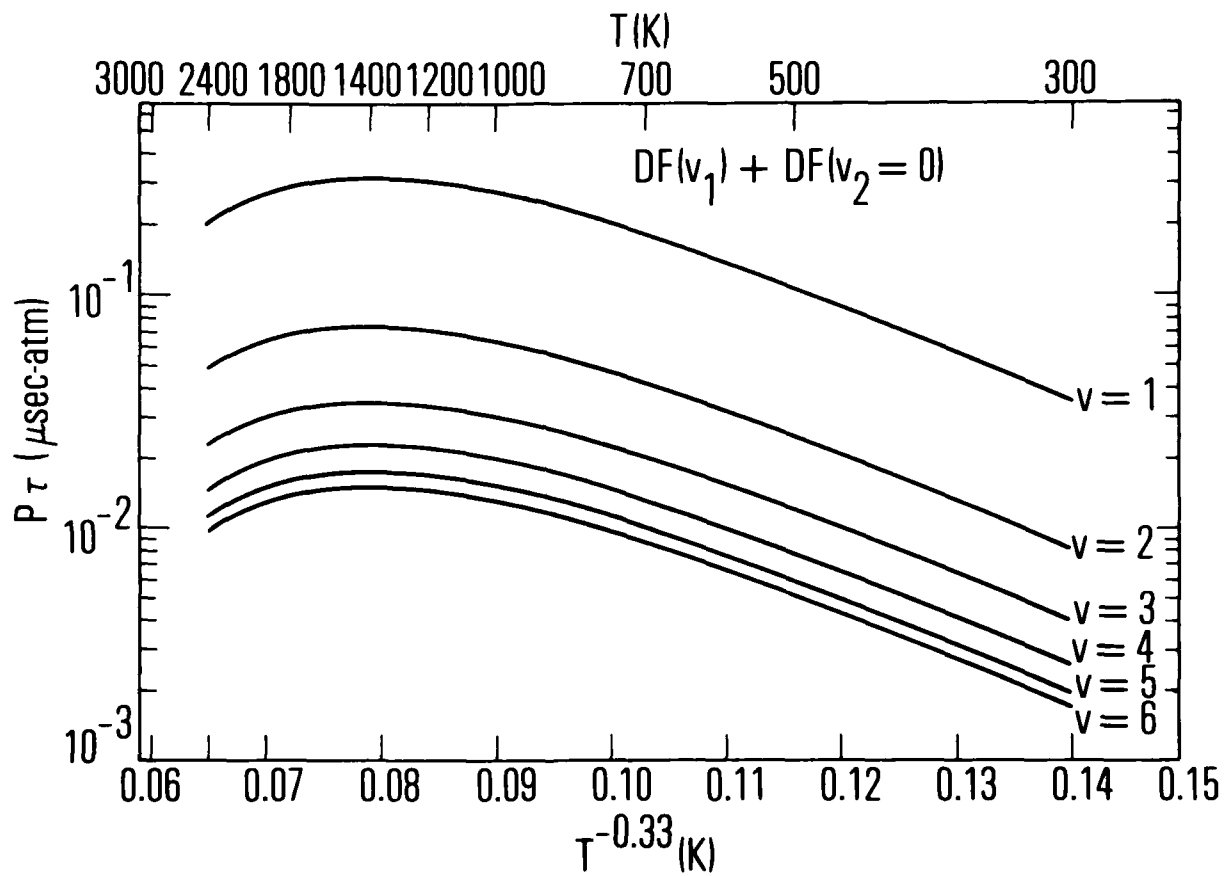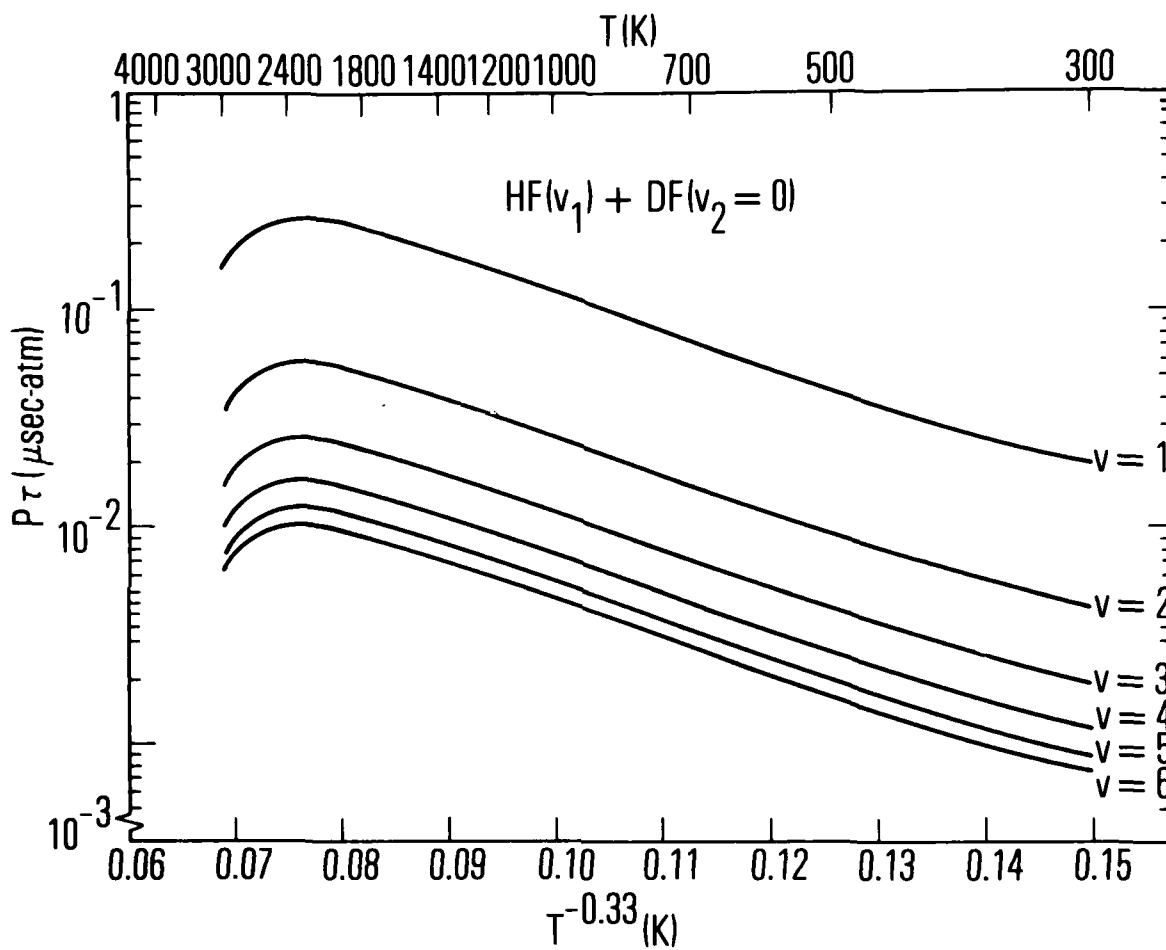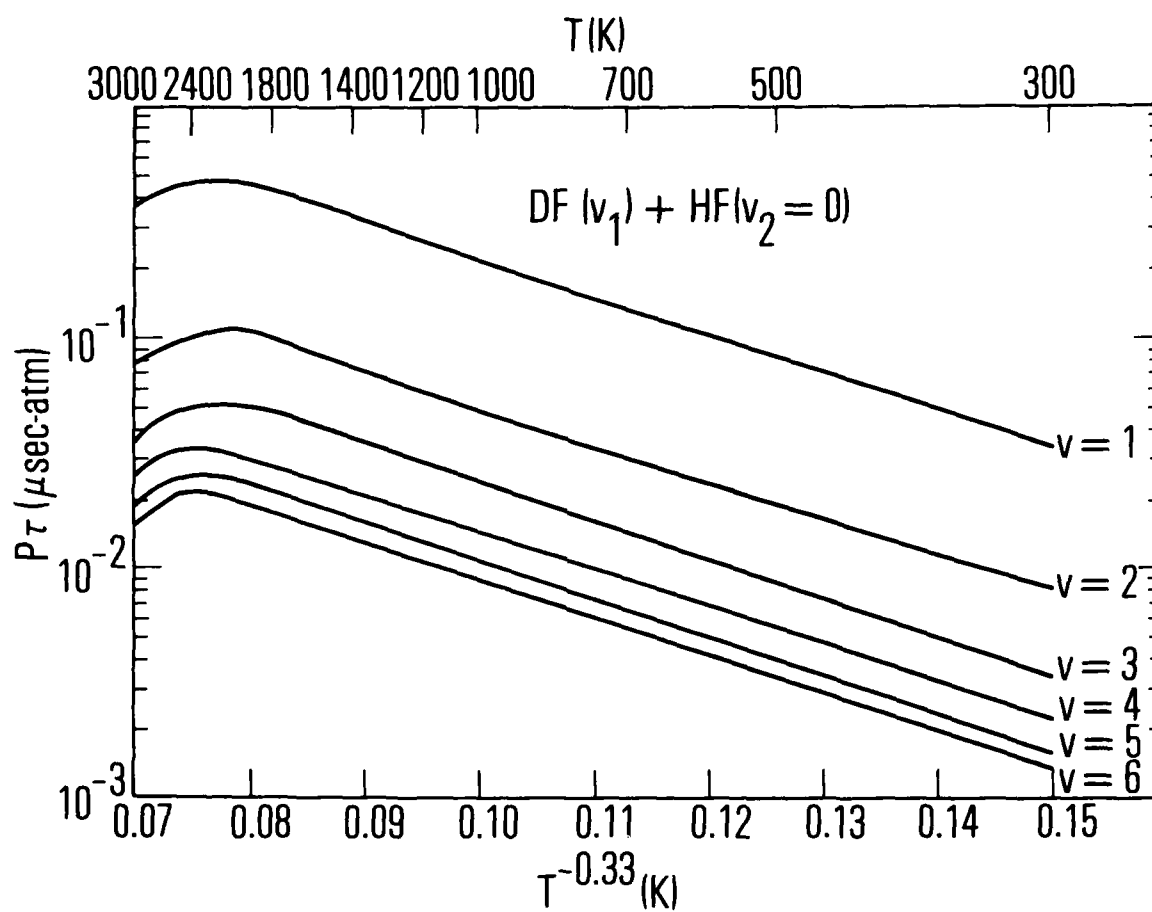used in this paper predicts a temperature dependence for relaxation from the upper vibrational levels similar to that obtained for relaxation from the $v = 1$ level. There are insufficient experimental data to substantiate this prediction of temperature dependence for vibrational relaxation from the upper vibrational levels. A comparison of the ratios $k_{vR}(v)/k_{vR}(v = 1)$ for the V → R processes indicates that the rate coefficients for deactivation from the upper v levels scale as v^n with n varying from 2.3 to 1.6 as v varies from 2 to 6. The actual values of n obtained from this model for the four isotopic systems of $HF(v_1) + HF(v_2 = 0)$ are given in Table II. The index n is not a constant for all v. The model predicts only a slight increase in rate coefficients for V → R relaxation as v increases beyond $v = 5$. This model indicates that the exponent n is not a constant, but decreases as v increases. The experimental values of n are obtained from total decay quenching coefficients which include contributions from both V → V and V → R processes. The v^n scaling employed in our model refers only to V → R processes. The V → V contribution can decrease or increase with increasing v, depending mainly on the behavior of the energy defects with increasing v. The v^n scaling for V → R processes is expected to exist even in systems where initially, at low v, the contribution from V → R processes is extremely small compared with the contributions from V → V processes. Table III provides a comparison of total deactivation rates at room temperature for the $HF(v_1) + HF(v_2 = 0)$ system. The results of Kwok and Wilkins[7] for $v = 2$ to 3 are in good agreement with those of Airey and Smith[4] and Poole and Smith,[5] while the results of Osgood, Sackett, and Javan[10] are a factor of 2 larger. The $v = 4$

TABLE II. V-dependence of $V \to R$ rate coefficients, values of superscript "n"

$$k^{V \to R} = v^n k^{V \to R}_{1 \to 0}$$

	Systems			
v	HF(v) + HF(0)	DF(v) + HF(0)	HF(v) + DF(0)	DF(v) + DF(0)
2	2.3	2.2	2.2	2.1
3	2.1	2.1	2.1	2.0
4	2.0	1.8	2.0	1.9
5	1.9	1.7	1.9	1.8
6	1.8	1.6	1.8	1.7

TABLE III. Comparison of quenching coefficients at T = 300 K for the HF(v_1) + HF (v_2 = 0) system[a]

V = 1	2	3	4	5	6	References
		$K_{HF}(v)$, 10^{12} cm^3/(mole sec)				
Experiments						
1.	16.0	31.0	28.0			10
	9.9	15.7	16.3			7
		11.0		35.0	61.0	22
	7.8	11.4	19.3	27.7	31.3	5
		16.9	43.4			3
1.1	9.6					1a
	11.0	12.0	>32.0	>48.0		4
						2
Theory						
0.49	3.9	6.0	11.4	16.3	25.9	20
	13.3	14.5	12.0	7.8		19
1.1	13.3	12.7	13.3	19.3		21
This model						
1.0	13.4	17.5	19.9	25.1	30.8	

[a]These rate coefficients represent the decay rates that result from both V → V and V → R energy-transfer processes.

level can be considered pivotal for determining a scaling trend in v^n, since $V \rightarrow$ R processes are considered dominant over $V \rightarrow V$ processes (83% $V \rightarrow R$ processes according to Table IV). However, the experimental results[3,4,5,7,10] vary over nearly a factor of 3. With higher v, any experimental scaling trend should be still more definitive, but results for a given v differ by a factor of 2.[4,5,7,22]

The model used here gives $HF(v_1) + HF(v_2 = 0)$ results which are in good agreement with the flow cell experimental measurements of Poole and Smith,[5] even to the trend of exponent n with increasing v. The model agrees qualitatively with Osgood[10] at v = 2, 3 but not at all at v = 4. More recent results[3,5,7,22] indicate that a coupling problem may exist on Osgood's v = 4 measurements. The results of Kwok and Wilkins[7] agree with the model, but those of Kwok and Cohen[23] do not. Both Airey[4] and Kwok[22] imply quantitatively larger quenching coefficients, and the results of Kwok[22] provide a nonvarying n with increasing v.

The model and virtually all experiments agree that the exponent n is approximately 2 and not unity. This value indicates that the quenching is a complex manifestation of several mechanisms and, therefore, cannot be understood as single quantum transfer between simple harmonic oscillators. The model framework demonstrates that this complexity in quenching coefficient behavior may be the integrated effect of many transfer channels and multiquantum sets of $V \rightarrow R$, $V \rightarrow V$, and $R \rightarrow R$, T mechanisms. Recently, Douglas and Moore[3] measured vibrational relaxation of HF(v = 3 and 4) by pumping HF directly from v = 0 to v = 4. Table III demonstrates that their value for the total decay rate from v = 4 is almost two and one-half times as

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TABLE IV. Percent Contribution of $v \to R$ energy transfer to the sum of the $(v \to v + v \to R)$ relaxation in $HF(v_1) + HF(v_2 = 0)$ collision

v	300 K	500 K	700 K	1000 K
2	37.0	42.6	45.2	48.5
3	70.3	73.9	73.5	76.2
4	83.4	86.0	85.3	87.9
5	92.4	93.9	93.6	94.3
6	96.1	96.7	96.5	96.8

large as its value from v = 3. Douglas and Moore found no evidence for multiquantum transitions in their study of vibrational relaxation of HF(v = 3, 4). They deduced that 75 to 95% of the HF(v = 4) must appear as HF(v = 3) by observing unresolved low J states and assuming rotational equilibrium. It is not clear if one can determine that the quenching process is a single vibrational quantum process by observing only the low J-state densities of HF in only the v = 3 and 4 levels.

The model results can be compared with available theoretical models.[19-21] In the Shin and Kim[19] model, it is assumed that only V → V transfer is important and that V → V transfer occurs in single-quantum transitions. At low temperatures, the model assumes a nonrigid dimer formation and at higher temperatures, complete rotational motion of the colliding molecules. The energy defect is removed by this rapid rotation. The total decay rate is the sum of the two mechanisms. The model used in this paper disagrees with the Shin and Kim predictions and predicts that V → R processes make considerable contributions to the total decay rates.

Billing and Poulsen[20] used a semiclassical approach to calculate rate coefficients for vibrational relaxation of HF(v) + HF(0) with v = 1 through 7. They treated the rotation and translation classically and vibrational energy transfer quantum mechanically. They found that orbiting collisions were important. Three-dimensional trajectory studies performed by Wilkins do not support their conclusion concerning the role of orbiting collisions at room temperature and above. Even though their model is different from our model, which predicts formation of high rotational states in the v manifolds, their model did predict that V → R processes make a dominant contribution to

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the total decay rates. Their absolute values of total decay rates were about 55% of the experimental values. However, it is important for the production of high rotational states to be investigated. Such states might indicate the validity of multiquantum vibration-rotation energy conversion. The model used by Billing and Poulsen[20] predicts single-quantum V → R energy-transfer.

Clendening et al.[21] used surprisal theory to calculate total decay rates for HF(v) + HF(0). This method allows them to include contributions from rate coefficients for several channels. The total deactivation rates agree well with the experimental data in Table III. Their total decay rates, however, scale linearly with v in the same way as an harmonic oscillator. The model presented here for V → R processes scales more rapidly with v. The Billing and Poulsen[20] model also indicates more rapid scaling with v than that indicated by Clendening et al.

Table IV lists the percentage of the total decay rates for HF(v) + HF(0) that corresponds to V → R energy transfer. At 300 K, this percentage increases from 37% at v = 2 to 96% at v = 6. Since our V → V rates decrease with increasing temperature, the percentage contribution that results from V → R processes also increases with increasing temperature at a specific v level. At 1000 K, the percentage contribution to the total decay rate that results from V → R processes increases from 49% at v = 2 to 97% at v = 6. These results have not been verified experimentally. Table IV indicates that as v increases, the main contribution to the total decay rate comes from V → R processes and not from the V → V processes. This conclusion was reached experimentally by Kwok and Wilkins[7] and Poole and Smith[5] while analyzing their flow-tube experiments, and theoretically by Billing and Poulsen.[20]   Table IV

indicates that at T = 300 K and v = 2, the contribution from V → V processes is approximately 63% of the sum $k_{vv} + k_{vR}$. With increasing v, however, the V → R processes dominate. A previous trajectory study by Wilkins[17] predicted that the V → V rate coefficients for HF(v) + HF(v = 0) collisions decrease as v increases. The net result is that both theoretical and experimental determinations for HF(v) + HF(0) collisions agree that the V → V contributions to the total decay rate coefficients decrease with increasing v.

Table V provides a comparison of the total decay rates obtained from this model with available experimental data for the HF + DF, DF + DF, and DF + HF systems. The values measured by Kwok[22] for HF(v) + DF at v = 5 and 6 are a factor of 2 larger than the model predictions. For the DF(v) + DF system at v = 2, the comparison between this model and experiment is good. At low v for the DF(v) + HF system, the model predictions are in good agreement with experimental results of Bott[25] and Kwok and Wilkins.[7] At high v the model predictions are almost a factor of 2 larger than the measurements of Poole and Smith.[5] To the best of our knowledge, Table V gives all the experimental data available on deactivation rates from the upper v levels for the three systems HF + DF, DF + DF, and DF + HF. The model has been used to calculate temperature-dependent rate coefficients for the V → R processes for these three systems; the results are given in Figs. 3 through 5. These results should be very useful for the modeling of either HF or DF chemical lasers.

TABLE V. Comparison of HF-DF, DF-DF and DF-HF total relaxation rates at T = 300 K

| | $k_T(v)$, 10^{12} cm^3/(mole sec) | | | | | | |
v = 1	2	3	4	5	6	Reference
HF(v) + DF						
	3.2	12.0		47.0	70.0	22
1.3	6.0	13.1	21.0	28.0	33.0	This Model
DF(v) + DF						
	12.9					23
	11.0					24
	11.6	13.8	16.9	19.9	24.8	This Model
DF(v) + HF						
1.2	1.6					4
		3.3	4.2	4.9		5
0.7						1b
0.8						1f
1.0	2.8	5.0				7
0.7	2.4	5.6				25
0.6	2.7	5.9	7.5	8.4	9.1	This Model

IV. CONCLUSIONS

The room temperature quenching rate coefficients for relaxation from the upper vibrational levels of HF and DF have been successfully duplicated with good agreement with available experimental data. This agreement was obtained with the use of a rotational nonequilibrium model and rate coefficients computed by Wilkins.[15-17] The key processes are V $\not\rightarrow$ R and R $\rightarrow$ V mechanisms, which give the problem a multiple-channel nature. The model provided temperature-dependent quenching rate coefficients for relaxation of HF(v) and DF(v) by HF(v = 0) and DF(v = 0). The temperature dependence is predicted to be similar to that measured for HF(v = 1) + HF and its isotopic analogs. The results of this study indicate that HF(v) + HF(v = 0), DF(v) + DF(v = 0), DF(v) + HF(v = 0), HF(v) + DF(v = 0) all scale as v^n with n varying between 2.3 and 1.6 as v increases from 2 to 6. This scaling has not been verified experimentally for temperatures higher than room temperature. The scaling is applicable only to the V $\rightarrow$ R processes. (For example, in HF(v) + DF(v = 0), the V $\rightarrow$ V process was predicted to increase slightly with increasing v, but the V $\rightarrow$ R processes were found to scale similarly to those for HF(v) + HF(v = 0). With the appropriate fine structure rate coefficients, this model should be equally applicable to vibrational relaxations from the upper vibrational levels of other hydrogen-halide molecules. This theoretical study is the first in which the temperature dependence of the V $\rightarrow$ R rate coefficients for HF(v_1) + HF(v_2 = 0) and its isotopic analogs has been predicted over the entire temperature range from 300 to 2400 K.

For a given molecule such as HF(v), the insensitivity of quenching coefficient to value of the exponent n for a number of differing chaperones, the absolute value of n itself (near 2), and the insensitivity of the relative temperature dependence of the quenching coefficient regardless of v level all indicate that the previously observed quenching coefficient is not sensitive to details of process cross sections. There is a commonality in the details of the internal energy structure of the molecule. This implies that much of this type of energy exchange is intramolecular and that a large number of channels may be involved. Certainly, questions about the utility of the quenching coefficient in revealing the actual energy transfer processes can be raised.

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Appendix A. Rate Coefficients for $(R \to R', T')$, $v \to v'$, and $v \to R$ Energy Transfer in $HF(v_1 \leqslant 4) + HF(v_2 = 0)$ Collisions at $T = 300$ K

Rotational Relaxation $(R \to R', T')$

$$HF(v_1 \ J_1) + M \xrightarrow{k_f} HF(v_1, \ J_1 - 1) + M$$
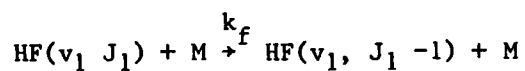
v_1	J_1	k_f, $10^{11} cm^3/(mole \ sec)$
0-4	1-5	20.0
0-3	6-10	10.0
0-3	11-15	5.0
0-2	16-20	2.5
0-1	21-25	1.25
0	26-30	0.625

Vibrational Relaxation $(v \to v')$

$$HF(v_1, \ J_1) + HF(v_2 = 0, \ J_1) \underset{k_b}{\overset{k_f}{\rightleftarrows}} HF(v_1 - 1, \ J_1) + HF(v_2 = 1, \ J_1)$$
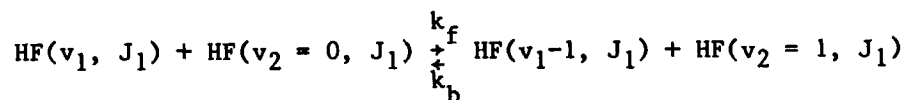
v_1	J_1	k_f, $10^{12} cm^3/(mole \ sec)$	k_b, $10^{12} cm^3/(mole \ sec)$
2	0-5	8.5	12.0
3	0-5	5.2	7.8
4	0-5	3.3	5.0

Vibrational Relaxation (v → R)

$$HF(v_1, J_1) + M_1 \xrightarrow{k_f} HF(v_1', J_1') + M_1$$
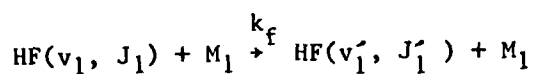
v_1	J_1	v_1'	J_1'	k_f, $10^{10} cm^3/(mole\ sec)$
1	0	0	10-16	1.2
1	1	0	10-16	6.2
1	2	0	10-16	12.0
1	3	0	10-16	8.7
1	4	0	10-16	4.9
1	5	0	10-16	4.9
2	0	1	10-16	6.9
2	1	1	10-16	34.0
2	2	1	10-16	69.0
2	3	1	10-16	49.0
2	4	1	10-16	28.0
2	5	1	10-16	28.0
2	0	0	16-21	4.6
2	1	0	16-21	22.0
2	2	0	16-21	43.0
2	3	0	16-21	30.0
2	4	0	16-21	17.0
2	5	0	16-21	17.0
3	0	2	10-15	14.0
3	1	2	10-15	33.0
3	2	2	10-15	66.0
3	3	2	10-15	45.0
3	4	2	10-15	27.0
3	5	2	10-15	27.0
3	0	1	16-20	15.0
3	1	1	16-20	38.0
3	2	1	16-20	120.0
3	3	1	16-20	52.0
3	4	1	16-20	30.0
3	5	1	16-20	30.0
3	0	0	21-26	9.9
3	1	0	21-26	24.0
3	2	0	21-26	48.0
3	3	0	21-26	34.0
3	4	0	21-26	20.0
3	5	0	21-26	20.0
4	0	3	10-15	7.8
4	1	3	10-15	35.0

Vibrational Relaxation (v + R) (Continued)

$$HF(v_1, J_1) + M_1 \xrightarrow{k_f} HF(v_1^{'}, J_1^{'}) + M_1$$

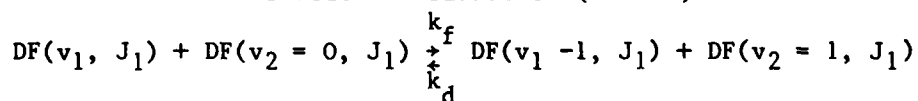| v_1	J_1	$v_1^{'}$	$J_1^{'}$	k_f, $10^{10} cm^3/(mole\ sec)$
4	2	3	10-15	70.0
4	3	3	10-15	49.0
4	4	3	10-15	28.0
4	5	3	10-15	28.0
4	0	2	15-20	5.8
4	1	2	15-20	29.0
4	2	2	15-20	58.0
4	3	2	15-20	41.0
4	4	2	15-20	23.0
4	5	2	15-20	23.0
4	0	1	20-25	3.7
4	1	1	20-25	19.0
4	2	1	20-25	37.0
4	3	1	20-25	26.0
4	4	1	20-25	14.0
4	5	1	20-25	14.0
4	0	0	25-30	4.1
4	1	0	25-30	21.0
4	2	0	25-30	41.0
4	3	0	25-30	29.0
4	4	0	25-30	16.0
4	5	0	25-30	16.0

Appendix B.   Rate Coefficients for $(R \to R', T')$, $v \to v'$, and $v \to R$
Energy Transfer in $DF(v_1 < 3) + DF(v_2 = 0)$ Collisions at
$T = 300$ K

Rotational Relaxation $(R \to R', T')$

$$DF(v_1, J_1) + M \xrightarrow{k_f} DF(v_1, J_1 - 1) + M$$
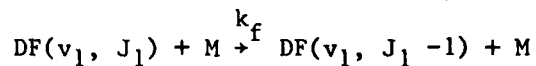
v_1	J_1	k_f, $10^{12} cm^3/(mole\ sec)$
0-4	1-5	15.0
0-3	6-10	7.5
0-3	11-15	3.75
0-2	16-20	1.875
0-1	21-25	0.9375
0	26-30	0.46875

Vibrational Relaxation $(v \to v')$

$$DF(v_1, J_1) + DF(v_2 = 0, J_1) \underset{k_d}{\overset{k_f}{\rightleftarrows}} DF(v_1 - 1, J_1) + DF(v_2 = 1, J_1)$$

v_1	J_1	k_f, $10^{12} cm^3/(mole\ sec)$	k_b, $10^{12} cm^3/(mole\ sec)$
2	0-5	10.6	13.2
3	0-5	6.5	8.6
4	0-5	4.1	5.5

Vibrational Relaxation (v → R)

$$DF(v_1, J_1) + M_1 \xrightarrow{k_f} DF(v'_1, J'_1) + M_1$$
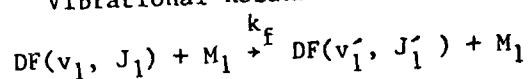
v_1	J_1	v'_1	J'_1	k_f, 10^{10} cm^3/(mole sec)
1	0	0	12–20	1.1
1	1	0	12–20	2.6
1	2	0	12–20	3.6
1	3	0	12–20	5.0
1	4	0	12–20	2.0
1	5	0	12–20	2.0
2	0	1	11–19	4.0
2	1	1	11–19	20.0
2	2	1	11–19	40.0
2	3	1	11–19	29.0
2	4	1	11–19	16.0
2	5	1	11–19	16.0
2	0	0	20–25	3.6
2	1	0	20–25	18.0
2	2	0	20–25	36.0
2	3	0	20–25	25.0
2	4	0	20–25	14.0
2	5	0	20–25	14.0
3	0	2	11–18	4.0
3	1	2	11–18	20.0
3	2	2	11–18	40.0
3	3	2	11–18	29.0
3	4	2	11–18	17.0
3	5	2	11–18	17.0
3	0	1	20–24	2.6
3	1	1	20–24	12.0
3	2	1	20–24	24.0
3	3	1	20–24	17.0
3	4	1	20–24	9.7
3	5	1	20–24	9.7
3	0	0	25–30	3.1
3	1	0	25–30	16.0
3	2	0	25–30	32.0
3	3	0	25–30	22.0
3	4	0	25–30	13.0
3	5	0	25–30	13.0